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Journal of Organometallic Chemistry 529 (1997) 205–213

Journal of Organometallic Chemistry

P–H bond activation of primary phosphine-boranes: access to α-hydroxy and α,α′-dihydroxyphosphine-borane adducts by uncatalyzed hydrophosphination of carbonyl derivatives

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Received 26 April 1996; revised 2 July 1996

Abstract

Primary P-phenyl and P-methyl phosphine-boranes **1** and **2** are prepared by complexation of the free phosphines with $BH_3 \cdot SMe_2$. They are stable and can be purified by distillation. Under basic conditions, they lead selectively to secondary alkylphosphine-boranes and under neutral conditions to the corresponding mono- and bis-hydroxyphosphine-boranes **5** and **6**. All these new compounds are purified by chromatography on silica gel. A competitive hydroboration induced by the decomplexation of BH_3 is observed as a minor process. Conditions for the decomplexation of phosphine-borane adducts are presented.

Keywords: Primary phosphine-boranes; Hydrophosphination; α-Hydroxyalkylphosphine-boranes; Hydroboration; P-alkylation

1. Introduction

Hydrophosphination of electrophiles such as aldehydes or ketones by secondary free phosphines is an important process which has been widely used for the preparation of functionalized phosphines. Addition reactions are usually performed under acidic or basic conditions or in the presence of radical initiators, for reviews see Ref. [1]. Preparation of some free tertiary α-hydroxyphosphines can also be achieved by addition of Ph_2PH on aldehydes under neutral conditions (PH activation by the two phenyl groups) [2]. Thus, addition of primary phosphines is usually more complex due to the low stability of the corresponding adducts: under acidic conditions, secondary phosphine oxides are formed as main products via an oxygen transfer [3]; under neutral conditions, the mono-α-hydroxyphosphines cannot be isolated and the α,α′-dihydroxyalkyl adducts are not always easy to purify since they easily dissociate, disproportionate and oxidize [4,5]. We have thought that activation and protection of the P–H bond by introduction of a borane (BH_3) on the phosphorus atom can bring an alternative route.

Activation of the P–H bond is an important process which has been applied during the last two decades to the synthesis of various functionalized phosphorus derivatives. Thus, the P–H acidifying effect induced by chloroalkyl groups or unsaturated fragments in primary or secondary phosphines is now well established. It allows us to perform the dehydrochlorination of α-chlorophosphines [6] and the base-induced rearrangement of vinyl- or ethynyl-phosphines [7,8] with Lewis bases under mild conditions. These reactions constitute two important routes to low coordinated phosphorus derivatives (phosphaalkenes, phosphaallenes or phosphaalkynes). Some aspects of this work have recently been reviewed [9,10].

In continuation of our interest in the development of P–H bond activation methodologies [6–8], we are now developing reactions which allow us to introduce under neutral conditions various functional groups on the phosphorus atom of primary phosphines (research of synthetic equivalents of $[R-P^{\ominus}_{\ominus}]$ and $[RP_{\ominus}-H]$). We describe in this paper the synthesis of two representative primary phosphine-borane derivatives (**1** and **2**) and our initial results bearing on their reactivity towards aldehydes and propanone. Hydrophosphination is the main process but a competitive hydroboration is also observed. The factors which control these two processes

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PII S0022-328X(96)06640-5

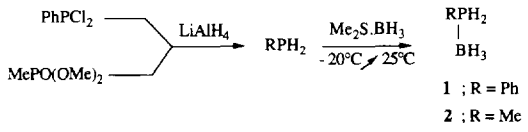
are analysed and the conditions to realize a mono- or a bis-addition are given. The synthetic interest of this methodology is estimated.

2. Results and discussion

Tertiary phosphine-boranes constitute an important class of organophosphorus compounds [11,12]. The BH_3 group of the phosphine complexes acts both as a protecting group (protection of the tricoordinated phosphorus atom) and as an activating group (C–H activation). This activation has allowed us to introduce various substituents and functional groups on the carbon in the α-position to the phosphorus atom. The nearly quantitative generation under mild conditions of the resulting functionalized free phosphines by treatment of the phosphine-borane adducts with an excess of amine makes this methodology attractive for the synthesis of new optically pure ligands [11]. As was initially demonstrated [12,13], the P–H bond of secondary phosphine-boranes is activated by the BH_3 group. However, the presence of KOH is needed to allow addition to electrophiles such as aldehydes or Michael acceptors [12]. The primary phosphine-boranes have aroused little attention from chemists. Only a few derivatives has been synthesized and fully characterized [13–15]. To our knowledge, the chemical reactivity of these species has not been studied so far.

2.1. Preparation of the primary phosphine-boranes 1 and 2

Primary phosphine-borane complexes have been poorly studied in the literature. This was attributed to their relatively low stability, mainly due to the presence of protic and hydridic hydrogen atoms within the same molecule [15]. We have chosen the primary phosphine-boranes **1** and **2** as representative derivatives of this class of compounds. They have been previously prepared in an analytical way by the reaction of the corresponding free phosphines with diborane [13]. Attempts to prepare them in a one-pot synthesis by reduction of the phosphonic esters with $LiAlH_4$–$NaBH_4$–$CeCl_3$ as a complex reducing system or by reduction of the dichlorophosphine with $LiAlH_4$ in the presence of BH_3/THF according to the procedures used for the preparation of tertiary phosphine-boranes [11,12] were unsuccessful. We have finally prepared them in a two-step procedure which involves the reduction of dichlorophenylphosphine or methylphosphonate with $LiAlH_4$ followed by complexation of the free phosphines with $Me_2S \cdot BH_3$ (Scheme 1). The phosphine-boranes **1** and **2** are stable and can be purified by sublimation (R = Ph) or distillation (R = Me) without decomposition. This approach can easily be scaled up to more than 15 g. Compounds are identified by comparison of the NMR data (^1H, ^{11}B, ^{31}P) with authentic samples [13]. They can be stored for a few months under neutral atmosphere without decomposition.



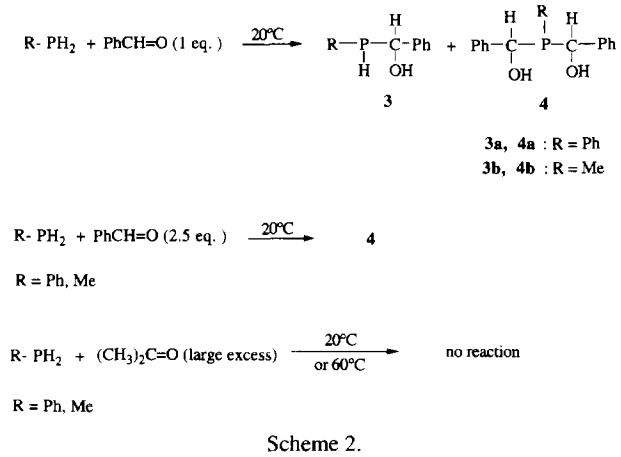
Scheme 1.

2.2. Reactivity of the free phosphines towards aldehydes and ketones

Bis-(hydroxyalkyl)phenylphosphines are synthesized in the literature by addition of aldehydes to the free phosphines in neutral media [4,5,16]. These compounds are however fairly stable, mainly when they are substituted. We have first tested the reactivity of the free phenyl- and methylphosphines towards the carbonyl derivatives (benzaldehyde and propanone). The reaction was monitored by ^{31}P NMR. Addition of phosphines to one equivalent of aldehyde gives a mixture of the mono- and bis-adducts **3** (**3a**, 47%; **3b**, 30%) and **4** (**4a**, 12%; **4b**, 40%) respectively. The bis-adducts **4** are solely observed by addition of an excess of reagent (2.5 equiv.). However, under the same conditions, no reaction was observed by addition of phenyl- or methylphosphines to propanone (Scheme 2). This last result is in good agreement with the literature: to our knowledge, additions of primary phosphines are only observed with activated ketones [17]. In Table 1, the ^{31}P NMR data of adducts **3** and **4** are collected and compared with analogous structures already described in the literature [5,18].

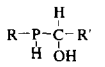
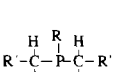
2.3. Metallation and subsequent alkylation of 1

Phosphine-borane **1** is metallated with a stoichiometric amount of ^nBuLi at −78 °C in THF (for a first



Scheme 2.

Table 1
^{31}P NMR data of mono- and bis-adducts of methyl- and phenylphosphine on carbonyl derivatives

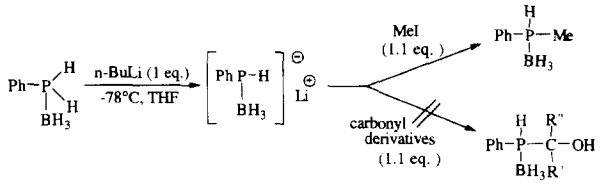
Entry		$\delta^{31}P$ ($^1J_{PH}$)		$\delta^{31}P$
1	R = R′ = Ph	−25.1 (211.2) −18.9 (211.3)	R = R′ = Ph	−4.4, 12.6, 12.8
2	R = Me, R′ = Ph	−55.2 (195.0) −53.9 (195.1)	R = Me, R′ = Ph	−21.1, −3.7, −2.6
			R = Ph, R′ = H	20 [a]
4			R = Ph, R′ = Me	−2, 12 [a]
5			R = Me, R′ = H	−36.9 [b]

[a] [5]; [b] [18].

alkylation of a primary phosphine-borane, see Ref. [19]). The generated phospha-anion is then allowed to react with various electrophiles such as methyliodide or carbonyl derivatives (1.1 equiv.). With methyliodide, the reaction proceeds smoothly and leads in high yield (85%) to the expected mono methylphosphine-borane together with a small amount of the dimethyl derivative (< 5%). Since secondary phosphine-boranes can be easily deprotected with an excess of amine [12], this procedure can be considered as a useful and clean method to prepare secondary phosphines (synthetic equivalent of [$RP_{\ominus}$–H]). We have then tried to add carbonyl derivatives (benzaldehyde, propionaldehyde, propanone) to the phospha-anion. The result of these trials was not so satisfactory. Whatever the carbonyl derivatives, we never observed the formation of the expected α-hydroxyphosphines, solely the starting material was recovered (Scheme 3).

2.4. Reactivity of the phosphine-boranes 1 and 2 towards aldehydes and propanone

We have studied the reactivity of **1** and **2** towards carbonyl compounds. The reactions were monitored by ^{31}P NMR (see Schemes 4 and 5 for the presentation of the reactions involving aldehydes and propanone respectively, and Table 2 for a comparative study of the reactivity). These experiments were performed firstly with 1.1 equiv. of carbonyl compounds and then with an excess (2.5–3 equiv.) in order to prepare the mono- and bis-adducts respectively.



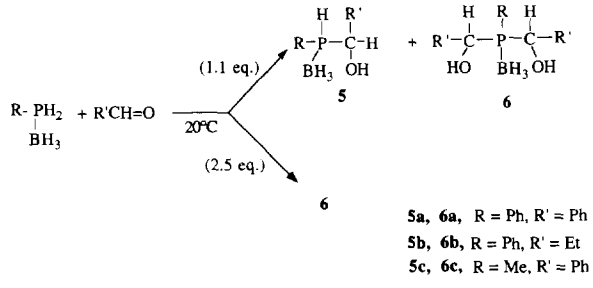
Scheme 3.

2.4.1. Results with 1.1 equiv. of carbonyl compounds

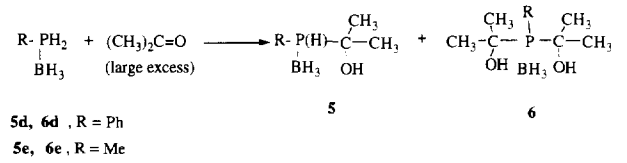
The addition of **1** and **2** to carbonyl compounds proceeds smoothly at room temperature. The hydrophosphination of propanone is however sluggish compared to that of aldehydes. The reactivity of the complexed phenylphosphine **1** appears weaker than that of its methyl counterpart **2**. As an example, **1** leads with benzaldehyde mainly to the mono-adduct (Table 2, entry 1, ratio 55/15), while **2** gives under the same conditions the bis-adduct as the major product (entry 3, ratio 8/46). A nearly similar result is observed in the reduction of propanone (entries 4 and 5). In all these reactions, free phosphine (RPH_2) is also observed; its amount is always higher starting from **1** (phosphine-borane bonded to a phenyl group) than from **2**. Thus, by reaction of **1** or **2** with benzaldehyde, 30% of $PhPH_2$ (entry 1) and only 12% of $MePH_2$ (entry 3) are respectively observed.

2.4.2. Results with 2.5–3 equiv. of carbonyl compounds

Addition of phosphine-boranes **1** and **2** to carbonyl derivatives is performed at room temperature. The reactions are followed by NMR and stopped after complete transformation of the phosphine-boranes **1** and **2**. In the case of aldehydes, the bis-adducts **6a–c** are the major products (reaction time 24 h). Only small amounts of the mono-adducts **5a–c** together with free phosphine



Scheme 4.



Scheme 5.

(RPH_2) are observed. The amount of free phosphine is lower in the case of the methyl derivative **2** (Table 2, entry 3, ratio **6c**/**5c** 92/6, 2% of free methylphosphine). For propanone, the hydrophosphination is sluggish: a mixture of the mono- and the bis-adducts, **5** and **6** respectively, is finally observed when the reactions are stopped after 15 days. The concentration of the free phosphines is high, mainly with the phenyl derivative **1** (40%). Less than 5% of the bis-adduct **6d** is finally obtained with **1** but the bis-adduct **6e** is the major product (44%) with **2**.

2.4.3. Preparative hydrophosphination of carbonyl derivatives and characterization of adducts 5 and 6

Preparative reactions have allowed us to isolate on gram scale, by chromatography on silica gel, the mono- and bis-adducts of the carbonyl derivatives. The conditions for the preparation of the mono- and the bis-adducts of aldehydes (compounds **5a–5c**, **6a–6c** respectively) are identical to those described in the analytical approach (Table 2). The adducts of propanone (compounds **5d**, **5e** and **6d**, **6e**) were prepared by a modification of the previously described procedure: the free phosphine released in the course of the reaction was recomplexed with an excess of $BH_3 \cdot SMe_2$, the amount of this reagent being adapted for each experiment. The mono-adducts **5d**, **5e** are thus obtained at room temperature, and the bis-adducts **6d**, **6e** upon heating the solution at 60 °C for 24 h. The observed yields (ca. 90% for **5d**, **5e**, **6e**, but only 5% for **6d**) are calculated from the phosphine-boranes **1** and **2**. A slight decomposition is observed during the chromatography (ca. 10–20%) mainly due to retro-addition reactions. The different stereomers have not been separated. All the purified compounds are stable in the pure form at room temperature. They constitute the first α-mono- and α,α′-bis-hydroxyphosphine-boranes described until now. Compounds **5a**, **5c–e** and **6a–e** have been fully characterized by ^{11}B, ^{31}P, ^{1}H and ^{13}C NMR. The mono-adduct **5b** was obtained in low yield and consequently has not been fully characterized. All the data are in agreement with the expected values. The characteristic ^{31}P, ^{11}B chemical shifts and $^{1}J_{PB}$, $^{1}J_{PH}$ coupling constants are collected in Table 3.

2.5. Mechanistic considerations, hydrophosphination vs. hydroboration

It was mentioned in the literature that the P–B bond strength decreases in concert with the value of the $^{1}J_{P-B}$ coupling constant [20]. Thus, $PH_3 \cdot BH_3$ ($^{1}J_{P-B}$ = 27 Hz) is observed in solution but is completely dissociated in the gas-phase, while $Me_3P \cdot BH_3$ ($^{1}J_{P-B}$ = 64 Hz) is, under the same conditions, a stable complex [21]. We observed in this work that the coupling constant of **1** is lower than that of **2** ($^{1}J_{P-B}$ = 38.4 Hz for **1** and $^{1}J_{P-B}$ = 41.8 Hz for **2**, Table 3). We consequently assume that the P–B bond strength of **1** is weaker than that of **2**. This assertion is verified by the fact that we always observed in our reactions a higher rate of decomplexation with the P-phenylphosphine-borane **1**.

As we have already mentioned in Sections 2.4.1 and 2.4.2, the substituent on phosphorus of phosphine-boranes **1** and **2** controls the reactivity of these substrates towards carbonyl derivatives. A higher reactivity in hydrophosphination reactions is observed for the methyl complex **2**. This result is unexpected since activation of the P–H bond is higher for the phenyl group (negative inductive effect of the phenyl substituent). We explain this lower reactivity by the higher rate of decomplexation of **1** induced by a lower P–B bond

Table 2
Reactivity of phosphine-boranes **1** and **2** towards aldehydes and propanone [a]

Entry	Phosphine-boranes	Carbonyl compounds	1.1 equiv. of carbonyl compounds (RPH_2)	2.5–3 equiv. of carbonyl compounds (RPH_2)
1	**1**	PhCHO	**5a** [b]: 55; **6a** [b]: 15 (30)	**5a** [c]: 20; **6a** [c]: 70 (10)
2	**1**	EtCHO	**5b** [b]: 4; **6b** [b]: 48 (18)	**5b** [c]: 5; **6b** [c]: 75 (20)
3	**2**	PhCHO	**5c** [b]: 8; **6c** [b]: 46 (12)	**5c** [c]: 6; **6c** [c]: 92 (2)
4	**1**	$(CH_3)_2C=O$	**5d** [d]: 14; **6d** [d]: 0 (20)	**5d** [e]: 55; **6d** [e] < 5 (40)
5	**2**	$(CH_3)_2C=O$	**5e** [f]: 8; **6e** [f]: 12 (8)	**5e** [e]: 41; **6e** [e]: 44 (15)

[a] Ratio (determination by ^{31}P NMR) of the different compounds present in the solution for reactions occurring at room temperature in the indicated reaction time.
[b] 1.1 equiv. of aldehyde (1 M), 1 day.
[c] 2.5 equiv. of aldehyde (1 M), 1 day.
[d] 1.1 equiv. of propanone (1.1 M), 1 day.
[e] 3 equiv. of propanone (1.1 M), 15 days.
[f] 1.1 equiv. of propanone (1.3 M), 4 days.

Table 3
^{31}P and ^{11}B NMR data of phosphine-boranes **1**, **2**, **5a–e** and **6a–e**

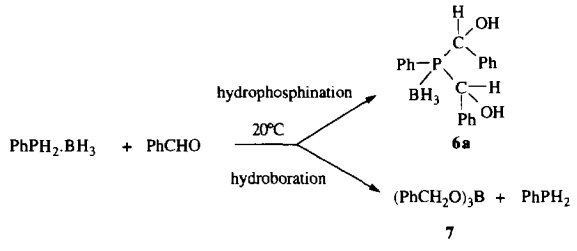
Compounds	$\delta\ ^{31}P\ (^{1}J_{PH})$	$\delta\ ^{11}B\ (^{1}J_{PB})$	$\delta\ ^{1}H$ of the P–H hydrogen
1	−46.9 (369.9)	−42.2 (38.4)	5.5
2	−66.7 (366.6)	−41.3 (41.8)	4.5
5a	18.3 (350.4) 19.5 (365)	−42.2 [a] (54.1)	5.4
5b [b]	10.1 (378)		
5c	2.6 (367.2) 4.0 (365.7)	−41.6 [a] (55.6)	4.7
5d	26.8 (376)	−42.8 (52.7)	5.2
5e	10.1 (359)	−41.7 (54.4)	4.55
6a	28.9, 30.2, 31.6	−42.1 [a,c]	
6b	23.2, 25.4, 27.7	−44.5 [a,c]	
6c	28.7, 31.7, 32,2	−41.4 [a,c]	
6d	40.5	−41.6 (65)	
6e	40.2	−41.3 (65.2)	

[a] The ^{11}B signal is too large to allow differentiation of isomers.
[b] The concentration of the mono-adduct **5b** is low and consequently it has not been characterized.
[c] Broad singlet.

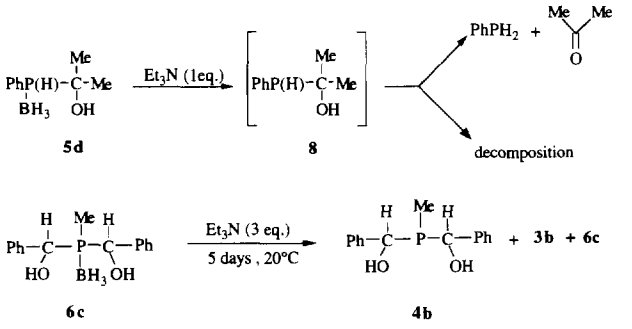
strength. The released borane can either recomplex the free phosphine (decomplexation/recomplexation equilibrium in the media) or react with the carbonyl derivative as a classical hydroborating agent. As an example, the reduced product (trialkylborate **7**) is identified in the reaction between **1** and benzaldehyde by comparison of its ^{11}B, ^{1}H and ^{13}C NMR data with those of an authentic sample (for a review on hydroboration see for example Ref. [22]) (Scheme 6). The ratio hydrophosphination/hydroboration is consequently dependent on the strength of the P–B bond and on the kinetics of these two competitive reactions. In all these experiments, hydrophosphination is however the major process.

2.6. Decomplexation of phosphine-boranes

Tertiary phosphine-boranes are considered in the literature as protected free phosphines [12], the boronato group being removed upon treatment with a large excess of amine. The deprotection of the different α-hydroxyphosphine-borane adducts **5** and **6** may offer a possible route to the corresponding free phosphines which are not accessible by other methods. Attempts to obtain the secondary hydroxyphosphine **8** by treatment



Scheme 6.



Scheme 7.

of the phosphine-borane precursor **5d** with triethylamine (1 equiv.) at room temperature (24 h) led to a complex mixture in which $PhPH_2$ is the major product (57%). We assume that the first step of the reaction is the deprotection, followed by the decomposition of the resulting free phosphine **8** which mainly occurred by retro-addition. Treatment of the bis-adduct **6c** with 3 equiv. of triethylamine (20 °C) leads as expected to the functionalized free phosphine **4b** (40%) accompanied, however, by the primary adduct **3b** (16%) and by the starting material **6c** (Scheme 7). We are currently trying to find better decomplexation conditions.

Alkylation experiments mentioned above (Section 2.3) confirm the low stability of dihydroxyphosphine adducts in basic media: if the P-alkylation is observed by treatment of **1** with $^{n}BuLi$ and quenching of the resulting phospha-anion with an alkylating agent (MeI), the expected adducts to benzaldehyde or propanone are not observed, solely the starting material is recovered. The retro-addition is probably the major process (Scheme 7).

3. Conclusion

We have presented in this work the synthesis of two representative primary phosphine-borane derivatives. These compounds which are easy to prepare and perfectly stable constitute interesting new tools in the field of organic chemistry. They can be considered as synthetic equivalents of $[RP_{\ominus}–H]$ via selective mono-alkylation/deprotection reactions and of $[R–P^{\ominus}_{\ominus}]$ via α,α′ bis-hydrophosphination/deprotection reactions. The hydrophosphination reactions occur smoothly at room temperature without any catalyst. The P–H activation induced by the BH_3 group is observed in the preparation of the propanone adducts (unactivated ketone). If hydrophosphination is the major process in all the reactions with aldehydes and propanone, a competitive hydroboration reaction has also been observed as a minor process. Addition of primary phosphine-borane derivatives to other electrophiles is currently under progress.

4. Experimental

All reactions were carried out under an atmosphere of nitrogen by using standard inert-atmosphere and Schlenk techniques. Benzene, diethylether, THF, toluene and tetraglyme were distilled prior to use from Na/benzophenone under nitrogen. Dichloromethane was distilled over $CaCl_2$. ^1H, ^{13}C, ^{31}P, ^{11}B spectra were recorded on a Bruker AM 300 or a Bruker AC 300. Mass spectra were obtained on a Varian Mat 311 instrument.

4.1. Synthesis of phenyl- and methylphosphines

Phenylphosphine is prepared by slow addition of a tetraglyme solution (50 ml) of dichlorophenylphosphine (12.1 g, 67.6 mmol) to lithium aluminium hydride (3.0 g, 79 mmol) dissolved in 100 ml of tetraglyme at −5 °C. The reaction mixture is then allowed to reach room temperature and stirred for 1 h. The mixture is then placed under vacuum and phosphine is separated from excess $LiAlH_4$ and tetraglyme by trap to trap distillation. The pure phenylphosphine is obtained in ca. 83% yield.

^{31}P NMR ($CDCl_3$) δ: −121.6 (t, $^1J_{PH}$ = 198.5 Hz).

Methylphosphine is prepared according to the same procedure starting from the commercially available dimethylmethylphosphonate (15.1 g, 121 mmol) and lithium aluminium hydride (5.8 g, 153 mmol). The reaction temperature is maintained at −20 °C. The pure methylphosphine is thus obtained in ca. 80–90% yield after purification by trap to trap distillation (see above).

^{31}P NMR (C_6D_6/THF) δ: −161.6 (t, $^1J_{PH}$ = 189.9 Hz).

4.2. Synthesis of phosphine-borane complexes 1 and 2

Dimethylsulfide borane (10.5 mmol, 1 ml) is slowly added to phosphine (10 mmol) dissolved in 15 ml of THF cooled to −20 °C. The reaction mixture is allowed to reach room temperature and stirred for 20 min. The crude product is obtained in essentially quantitative yield. Purification of **1** and **2** is performed by sublimation for **1** and distillation for **2** under vacuum. The phosphine-borane complexes are stable for a few months under a nitrogen atmosphere.

1: sublimation temperature 90 °C (0.4 mmHg), m.p. 50 °C, 95% yield. ^{31}P NMR ($CDCl_3$) δ: −46.95 (td, $^1J_{PH}$ = 369.9 Hz, $^1J_{PB}$ = 38.4 Hz). ^{11}B NMR ($CDCl_3$) δ: −42.2 (qd, $^1J_{BH}$ = 101.6 Hz, $^1J_{PB}$ = 38.4 Hz). ^1H NMR ($CDCl_3$) δ: 0.92 (q, $^1J_{BH}$ = 101.6 Hz, 3H, BH_3), 5.51 (dm, $^1J_{PH}$ = 369.9 Hz, 2H, P–H), 7.30–7.60 (m, 3H, $H_{arom.}$), 7.60–7.85 (m, 2H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 119.87 (d, $^1J_{CP}$ = 53.5 Hz, P–$C_{quat.}$), 129.27 (dd, $^1J_{CH}$ = 166.7 Hz, $^3J_{CP}$ = 10.3 Hz, C_{meta}), 132.08 (dd, $^1J_{CH}$ = 161.6 Hz, $^4J_{CP}$ = 2.3 Hz, C_{para}), 133.77 (dd, $^1J_{CH}$ = 165.8 Hz, $^2J_{CP}$ = 9.3 Hz, C_{ortho}). HRMS: [M − BH_3]$^+$ found 110.0273; calc. 110.0285.

2: b.p. 100 °C (30 mmHg), 80% yield. ^{31}P NMR ($CDCl_3$) δ: −66.67 (tq, $^1J_{PH}$ = 366.6 Hz, $^1J_{PB}$ = 41.8 Hz). ^{11}B NMR ($CDCl_3$) δ: −41.29 (qd, $^1J_{BH}$ = 99.5 Hz, $^1J_{PB}$ = 41.8 Hz). ^1H NMR ($CDCl_3$) δ: 0.56 (q, $^1J_{BH}$ = 99.5 Hz, 3H, BH_3), 1.38 (dt, $^2J_{PH}$ = 12 Hz, $^3J_{HH}$ = 6.6 Hz, 3H, P–CH_3), 4.54 (dm, $^1J_{PH}$ = 366.6 Hz, 2H, P–H). ^{13}C NMR ($CDCl_3$) δ: 0.26 (qd, $^1J_{CH}$ = 133 Hz, $^1J_{CP}$ = 38.5 Hz, P–CH_3). HRMS: [M − H$^\cdot$]$^+$ found 61.038; calc. 61.0378.

4.3. Hydrophosphination of the free phenyl- and methylphosphine

Benzaldehyde or propanone (1 or 2.5 equiv.) is added to a 1 M toluene solution of free phosphine (1 mmol). The mixture is stirred at room temperature and the reaction monitored by ^{31}P NMR. For 1 equiv. of benzaldehyde, the reaction is complete in 1 day, leading to a mixture of mono- and bis-adduct **3** (**3a**, 47%; **3b**, 30%) and **4** (**4a**, 12%; **4b**, 40%) respectively. With 2.5 equiv. of benzaldehyde, only the bis-adduct **4** is observed. For propanone, no reaction is observed even after heating the solution for 24 h at 60 °C.

3a: $PhPH_2$ (1 mmol, 0.11 ml), benzaldehyde (1 equiv., 1 mmol, 0.1 ml), 24 h at 20 °C. Two diastereomers. ^{31}P NMR ($CDCl_3$) δ: −25.1 (d, $^1J_{PH}$ = 211.2 Hz), −18.9 (d, $^1J_{PH}$ = 211.3 Hz).

3b: $MePH_2$ (1 M in ether, 1 mmol, 1 ml), benzaldehyde (1 equiv., 1 mmol, 0.1 ml), 24 h at 20 °C. Two diastereomers. ^{31}P NMR ($CDCl_3$) δ: −55.2 (d, $^1J_{PH}$ = 195 Hz), −53.9 (d, $^1J_{PH}$ = 195 Hz).

4a: $PhPH_2$ (1 mmol, 0.11 ml), benzaldehyde (2.5 equiv., 2.5 mmol, 0.25 ml), 24 h at 20 °C. Three diastereomers. ^{31}P NMR ($CDCl_3$) δ: −4.4 (s), 12.6 (s), 12.8 (s).

4b: $MePH_2$ (1 M in ether, 1 mmol, 1 ml), benzaldehyde (2.5 equiv., 2.5 mmol, 0.25 ml), 24 h at 20 °C. Three diastereomers. ^{31}P NMR ($CDCl_3$) δ: −21.1 (s), −3.7 (s), −2.6 (s).

4.4. Alkylation of phenylphosphine-borane 1

Phenylphosphine-borane **1** (1.6 mmol, 0.2 g) in 3 ml of freshly distilled THF is cooled to −85 °C (internal temperature). n-Butyllithium (1.6 M, 1.05 equiv., 1.05 ml) is then slowly added and the mixture is stirred at this temperature for 10 min before addition of methyliodide (1.1 equiv., 1.75 mmol, 0.11 ml). The reaction mixture is allowed to slowly reach room temperature and is then stirred for 2 h at this temperature. Hydrolysis of the mixture is performed at 0 °C with 0.2 ml of degassed water. The organic layer is dried over $MgSO_4$, filtered and the solvents are evaporated under vacuum. Yield of crude product (90%). ^{31}P NMR ($CDCl_3$) δ:

−16.04 (dq, $^1J_{PH}$ = 375.9 Hz, $^1J_{PB}$ = 57 Hz). ^{11}B NMR ($CDCl_3$) δ: −40.1 (qd, $^1J_{BH}$ = 96.3 Hz, $^1J_{PB}$ = 57 Hz). ^{1}H NMR ($CDCl_3$): δ 0.50 (q, $^1J_{BH}$ = 100.0 Hz, 3H, BH_3), 1.32 (dd, $^2J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 6.15 Hz, 3H, P–CH_3), 5.34 (dm, $^1J_{PH}$ = 375.9 Hz, 1H, P–H), 7.13–7.24 (m, 3H, $H_{arom.}$), 7.38–7.49 (m, 2H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 8.23 (qd, $^1J_{CH}$ = 136.3 Hz, $^1J_{CP}$ = 38.8 Hz, P–CH_3), 126.27 (dm, $^1J_{CP}$ = 56.6 Hz, P–$C_{quat.}$), 128.90 (dd, $^1J_{CH}$ = 162.8 Hz, $^3J_{CP}$ = 10.3 Hz, C_{meta}), 131.55 (dd, $^1J_{CH}$ = 161.7 Hz, $^4J_{CP}$ = 2.5 Hz, C_{para}), 132.20 (dd, $^1J_{CH}$ = 163.8 Hz, $^2J_{CP}$ = 9.2 Hz, C_{ortho}).

4.5. Hydrophosphination reactions

4.5.1. Mono-adducts

The electrophile derivative (approximately 1.1 equiv.) is slowly added to phosphine-borane **1** or **2** (7 mmol) in a benzene or a toluene solution (1 M for **1** and 1.5 M for **2**). The mixture is stirred at room temperature. The reaction is monitored by ^{31}P NMR. When the precursor is consumed, the solvent is removed under vacuum and the new product is purified by silica-gel chromatography.

5a: phenylphosphine-borane **1** in toluene (1 M), benzaldehyde (1.05 equiv., 0.75 ml), 24 h at 20 °C, $R_{f(CH_2Cl_2)}$ = 0.6, yield of pure product 30% (viscous oil). The ^{1}H and ^{13}C NMR data are only given for the major adduct. ^{31}P NMR ($CDCl_3$) δ: 18.3 (qd, $^1J_{PH}$ = 350.4 Hz, $^1J_{PB}$ = 49.7 Hz) (45%), 19.5 (qd, $^1J_{PH}$ = 365 Hz, $^1J_{PB}$ = 54.1 Hz) (55%). ^{11}B NMR ($CDCl_3$) δ: −42.24 (qd, $^1J_{BH}$ = 100.5 Hz, $^1J_{PB}$ = 54 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.75 (m, 3H, BH_3), 3.56 (broad s, 1H, –OH), 5.36 (d, $^1J_{PH}$ = 365 Hz, P–H), 7–7.4 (m, 10H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 71.32 (ddm, $^1J_{CH}$ = 147.2 Hz, $^1J_{CP}$ = 28.6 Hz, P–CH–OH), 121.48 (m, P–$C_{quat.}$), 125.35 (ddm, $^1J_{CH}$ = 158.4 Hz, J_{CP} = 3.9 Hz, $C_{arom.}$), 126.75 (dm, $^1J_{CH}$ = 160.2 Hz, $C_{arom.}$), 127–127.70 (dm, $^1J_{CH}$ = 162.9 Hz, $C_{arom.}$), 131.05 (dm, $^1J_{CH}$ = 168.3 Hz, $C_{arom.}$), 133.08 (ddm, $^1J_{CH}$ = 162.5 Hz, J_{CP} = 8.4 Hz, $C_{arom.}$), 135.90 (m, C–$C_{quat.}$). HRMS: [M − H_2O] found 212.0905; calc. 212.0926.

5c: methylphosphine-borane **2** in toluene (1 M), benzaldehyde (1.05 equiv., 0.75 ml), 24 h at 20 °C, $R_{f(CH_2Cl_2)}$ = 0.49, yield of pure product 5% (viscous oil). ^{31}P NMR ($CDCl_3$) δ: 2.6 (dq, $^1J_{PH}$ = 367.2 Hz, $^1J_{PB}$ = 55.6 Hz) (52%), 4.0 (dq, $^1J_{PH}$ = 365.7 Hz, $^1J_{PB}$ = 55.6 Hz) (48%). ^{11}B NMR ($CDCl_3$) δ: −41.6 (qd, $^1J_{BH}$ = 98.0 Hz, $^1J_{PB}$ = 55.6 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.48 (q, $^1J_{BH}$ = 98.0 Hz, 6H, BH_3), 1.23 (dd, $^2J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, P–CH_3), 1.25 (dd, $^2J_{PH}$ = 11.1 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, P–CH_3), 2.80 (broad s, 2H, –OH), 4.69 (dm, $^1J_{PH}$ = 366.5 Hz, 2H, P–H), 5.07 (dd, $^3J_{HH}$ = 4.65 Hz, $^2J_{PH}$ = 2.6 Hz, 1H, P–C–*H*), 5.18 (dd, $^3J_{HH}$ = $^2J_{PH}$ = 3.63 Hz, 1H, P–C–*H*), 7.21–7.36 (m, 10H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 1.26 (qdm, $^1J_{CH}$ = 130.0 Hz, $^1J_{CP}$ = 35.2 Hz, P–CH_3), 2.02 (qdm, $^1J_{CH}$ = 133.2 Hz, $^1J_{CP}$ = 35.5 Hz, P–CH_3), 69.37 (ddm, $^1J_{CH}$ = 145.3 Hz, $^1J_{CP}$ = 42.0 Hz, P–*C*H), 70.27 (ddm, $^1J_{CH}$ = 148.1 Hz, $^1J_{CP}$ = 40.9 Hz, P–*C*H), 125.78 (ddm, $^1J_{CH}$ = 159.2 Hz, $^3J_{CP}$ = 3.7 Hz, C_{ortho}), 126.18 (ddm, $^1J_{CH}$ = 158.8 Hz, $^3J_{CP}$ = 3.8 Hz, C_{ortho}), 128.38 (dm, $^1J_{CH}$ = 160.4 Hz, C_{para}), 128.41 (dm, $^1J_{CH}$ = 160.4 Hz, C_{para}), 128.81 (dd, $^1J_{CH}$ = 161.2 Hz, $^4J_{CP}$ = 2.1 Hz, C_{meta}), 128.84 (dd, $^1J_{CH}$ = 161.2 Hz, $^4J_{CP}$ = 2.0 Hz, C_{meta}), 137.02 (dm, $^2J_{CP}$ = 2.4 Hz, $C_{quat.}$), 137.59 (dm, $^2J_{CP}$ = 3.0 Hz, $C_{quat.}$). HRMS: [M − H] found 167.081; calc. 167.0797.

5d: phenylphosphine-borane **1** in benzene (1.1 M), propanone (2.5 equiv., 1.3 ml), 4 days at 20 °C. In the course of the reaction, 0.4 equiv. of $BH_3 \cdot SMe_2$ is added in order to complex the free phenylphosphine which is released. $R_{f(CH_2Cl_2)}$ = 0.49, yield of pure product 50% (oil). ^{31}P NMR ($CDCl_3$) δ: 26.78 (qd, $^1J_{PH}$ = 376 Hz, $^1J_{PB}$ = 52.7 Hz). ^{11}B NMR ($CDCl_3$) δ: −42.8 (qd, $^1J_{BH}$ = 99.5 Hz, $^1J_{PB}$ = 52.7 Hz, BH_3). ^{1}H NMR ($CDCl_3$) δ: 0.72 (q, $^1J_{BH}$ = 99.5 Hz, 3H, BH_3), 1.33 (d, $^3J_{PH}$ = 12.6 Hz, 3H, CH_3), 1.40 (d, $^3J_{PH}$ = 13.4 Hz, 3H, CH_3), 2.11 (broad s, 1H, OH), 5.23 (dqm, $^1J_{PH}$ = 376 Hz, $^3J_{HH}$ = 6.8 Hz, P–H), 7.30–7.50 (m, 3H, $H_{arom.}$), 7.6–7.7 (m, 2H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 25.4 (qd, $^1J_{CH}$ = 128.1 Hz, $^2J_{CP}$ = 11.1 Hz, CH_3), 26.4 (qd, $^1J_{CH}$ = 128.1 Hz, $^2J_{CP}$ = 12.4 Hz, CH_3), 68.8 (d, $^1J_{CP}$ = 38.7 Hz, P–*C*–OH), 122.44 (d, $^1J_{CP}$ = 51.3 Hz, P–$C_{quat.}$), 124.94 (dd, $^1J_{CH}$ = 162.7 Hz, $^3J_{CP}$ = 9.7 Hz, C_{meta}), 131.15 (dd, $^1J_{CH}$ = 163.3 Hz, $^4J_{CP}$ = 2.55 Hz, C_{para}), 133.15 (dd, $^1J_{CH}$ = 163.2 Hz, $^2J_{CP}$ = 7.7 Hz, C_{ortho}).

5e: methylphosphine-borane **2** in benzene (1.3 M), propanone (3 equiv., 1.6 ml), 15 days at 20 °C, $R_{f(CH_2Cl_2/Et_2O,9/1)}$ = 0.5, yield of pure product 30% (pale yellow oil). ^{31}P NMR ($CDCl_3$) δ: 10.13 (qd, $^1J_{PH}$ = 359 Hz, $^1J_{BP}$ = 54.4 Hz). ^{11}B NMR ($CDCl_3$) δ: −41.68 (qd, $^1J_{BH}$ = 98.9 Hz, $^1J_{PB}$ = 54.4 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.42 (q, $^1J_{BH}$ = 98.9 Hz, 3H, BH_3), 1.33 (dd, $^2J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 6.1 Hz, 3H, P–CH_3), 1.40 (d, $^3J_{PH}$ = 13.4 Hz, 3H, C–CH_3), 1.45 ppm (d, $^3J_{PH}$ = 13.4 Hz, 3H, C–CH_3), 2.65 (broad s, 1H, –OH), 4.55 (dm, $^1J_{PH}$ = 359 Hz, 1H, P–H). ^{13}C NMR ($CDCl_3$) δ: 1.88 (qd, $^1J_{CH}$ = 132 Hz, $^1J_{CP}$ = 35.2 Hz, P–CH_3), 25.87 (qd, $^1J_{CH}$ = 127.7 Hz, $^2J_{CP}$ = 10.1 Hz, C–CH_3), 27.10 (qd, $^1J_{CH}$ = 128.0 Hz, $^2J_{CP}$ = 9.6 Hz, C–CH_3), 68.02 (d, $^1J_{CP}$ = 42.7 Hz, P–*C*–OH).

4.5.2. Bis-adducts

A small excess of the appropriate electrophile derivative (2.2 to 3 equiv.) is slowly added to phosphine-borane **1** or **2** (7 mmol) in a benzene or a toluene solution (1 M for **1** and 2 M for **2**). The mixture is stirred at room temperature except for acetone (60 °C). The reaction is monitored by ^{31}P NMR. When all the precursor is

consumed, the solvent is removed under vacuum and the new product purified by silica-gel chromatography.

6a: phenylphosphine-borane **1** in toluene (1 M), benzaldehyde (2.2 equiv., 1.6 ml), 24 h at 20 °C, $R_{f(CH_2Cl_2)}$ = 0.32, yield of pure product 65% (white solid). Three diastereomers, the ^1H and ^{13}C NMR data are only given for the major adduct. ^{31}P NMR ($CDCl_3$) δ: 28.9 (m) (5%), 30.2 (m) (20%), 31.6 (m) (75%). ^{11}B NMR ($CDCl_3$) δ: −42.12 (m). ^1H NMR ($CDCl_3$) δ: 0.5 (m, 3H, BH_3), 3.21 (broad s, 2H, OH), 5.47 (s, 2H, P–C*H*–OH), 7–7.20 (m, 10H, $H_{arom.}$), 7.20–7.35 (m, 3H, $H_{arom.}$), 7.65–7.80 (m, 2H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 72.75 (dd, $^1J_{CH}$ = 146.2 Hz, $^1J_{CP}$ = 33.2 Hz, P–*C*H–OH), 120.43 (d, $^1J_{CP}$ = 46.9 Hz, P–$C_{quat.}$), 126.34 (dd, $^1J_{CH}$ = 160.0 Hz, $^3J_{CP}$ = 4.2 Hz, $C_{ortho\ Ph-C}$), 126.94 (dd, $^1J_{CH}$ = 160.2 Hz, $^5J_{CP}$ = 2.1 Hz, $C_{para\ Ph-C}$), 127.18 (dd, $^1J_{CH}$ = 161.0 Hz, $^3J_{CP}$ = 9.8 Hz, $C_{meta\ Ph-P}$), 127.52 (dd, $^1J_{CH}$ = 162.2 Hz, $^4J_{CP}$ = 2.8 Hz, $C_{meta\ Ph-C}$), 131.25 (dd, $^1J_{CH}$ = 160.0 Hz, $^4J_{CP}$ = 2.5 Hz, $C_{para\ Ph-P}$), 134.18 (dd, $^1J_{CH}$ = 155.0 Hz, $^2J_{CP}$ = 8 Hz, $C_{ortho\ Ph-P}$), 135.33 (m, C–$C_{quat.}$).

6b: phenylphosphine-borane **1** in benzene (1 M), propionaldehyde (2.5 equiv., 1.3 ml), 24 h at 20 °C, $R_{f(CH_2Cl_2/Et_2O,3/1)}$ = 0.75, yield in pure product 70% (pale yellow oil). ^{31}P NMR ($CDCl_3$) δ: 23.2 (m) (12%), 25.4 (m) (28%), 27.7 (m) (60%). ^1H NMR ($CDCl_3$) δ: 0.65 (m, 9H, BH_3), 0.87 (t, $^3J_{HH}$ = 7.24 Hz, 6H, CH_3), 0.9 (t, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3), 0.91 (t, $^3J_{HH}$ = 7.3 Hz, 6H, CH_3), 1.26–1.58 (m, 6H, CH_2), 1.58–1.87 (m, 6H, CH_2), 3.65 (broad s, 6H, –P–C–O*H*), 4.27–4.50 (m, 6H, –P–C*H*–OH), 7.31–7.50 (m, 9H, $H_{arom.}$), 7.66–7.93 (m, 6H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 10.73 (qd, $^1J_{CH}$ = 126.6 Hz, $^3J_{CP}$ = 10.7 Hz, CH_3), 10.87 (qd, $^1J_{CH}$ = 126.6 Hz, $^3J_{CP}$ = 10.3 Hz, CH_3), 11.08 (qd, $^1J_{CH}$ = 126.6 Hz, $^3J_{CP}$ = 12.4 Hz, CH_3), 24.78 (td, $^1J_{CH}$ = 126.9 Hz, $^2J_{PC}$ = 4.7 Hz, CH_2), 25.22 (td, $^1J_{CH}$ = 127.5 Hz, $^2J_{PC}$ = 8.7 Hz, CH_2), 25.43 (td, $^1J_{CH}$ = 127.8 Hz, $^2J_{PC}$ = 4 Hz, CH_2), 69.17 (dd, $^1J_{CH}$ = 150 Hz, $^1J_{CP}$ = 44.1 Hz, –P–*C*H–OH), 70.24 (dd, $^1J_{CH}$ = 147 Hz, $^1J_{CP}$ = 37.3 Hz, –P–*C*H–OH), 72.60 (dd, $^1J_{CH}$ = 145 Hz, $^1J_{CP}$ = 37.8 Hz, –P–*C*H–OH), 122.97 (d, $^1J_{CP}$ = 48 Hz, $C_{quat.}$–P), 124.46 (d, $^1J_{CP}$ = 46.7 Hz, $C_{quat.}$–P), 126.13 (d, $^1J_{CP}$ = 47 Hz, $C_{quat.}$–P), 128.53 (dd, $^1J_{CH}$ = 161.3 Hz, $^3J_{CP}$ = 9.6 Hz, C_{meta}), 128.72 (dd, $^1J_{CH}$ = 161.3 Hz, $^3J_{CP}$ = 9.3 Hz, C_{meta}), 129.02 (dd, $^1J_{CH}$ = 161.3 Hz, $^3J_{CP}$ = 9.4 Hz, C_{meta}), 131.95 (dd, $^1J_{CH}$ = 144.2 Hz, $^4J_{CP}$ = 2.3 Hz, C_{para}), 132.87 (d, $^2J_{CP}$ = 7.8 Hz, C_{ortho}), 133.91 (dd, $^1J_{CH}$ = 154.3 Hz, $^2J_{CP}$ = 7.6 Hz, C_{ortho}), 134.79 (dd, $^1J_{CH}$ = 163.8 Hz, $^2J_{CP}$ = 7.7 Hz, C_{ortho}). The three p-aromatic carbons display the same chemical shift.

6c: methylphosphine-borane **2** in toluene (1.5 M), benzaldehyde (2 equiv., 1.4 ml), 24 h at 20 °C. A small quantity of $BH_3 \cdot SMe_2$ is added at the end of the reaction in order to complex the released free adduct if necessary. $R_{f(CH_2Cl_2)}$ = 0.2, yield in pure product 65% (white solid). Three diastereomers, the ^1H and ^{13}C NMR data are only given for the major adduct. ^{31}P NMR ($CDCl_3$) δ: 28.7 (m) (5%), 31.7 (m) (85%), 32.2 (m) (10%). ^{11}B NMR ($CDCl_3$) δ: −41.44 (qm, $^1J_{BH}$ = 96.9 Hz). ^1H NMR ($CDCl_3$) δ: 0.30 (m, 3H, BH_3), 0.98 (d, $^2J_{PH}$ = 9.9 Hz, 3H, P–C*H*$_3$), 1.90–2.50 (broad s, 2H, –OH), 4.44 (s, 2H, P–C–*H*), 7.22–7.29 (m, 10H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: −2.04 (qd, $^1J_{CH}$ = 135.0 Hz, $^1J_{CP}$ = 32.7 Hz, P–*C*H$_3$), 72.68 (dd, $^1J_{CH}$ = 149.1 Hz, $^1J_{CP}$ = 31.4 Hz, P–*C*H), 126.90 (ddm, $^1J_{CH}$ = 160.0 Hz, $^3J_{CP}$ = 4.0 Hz, C_{ortho}), 128.30 (ddm, $^1J_{CH}$ = 160.5 Hz, $^4J_{CP}$ = 2.2 Hz, C_{meta}), 128.57 (ddm, $^1J_{CH}$ = 160.3 Hz, $^5J_{CP}$ = 2.8 Hz, C_{para}), 136.50 (m, $C_{quat.}$).

6d: phenylphosphine-borane **1** in benzene (1.1 M), propanone (2.5 equiv., 1.3 ml), 4 days at 20 °C, $R_{f(CH_2Cl_2)}$ = 0.25, yield of pure product 5% (white solid). ^{31}P NMR ($CDCl_3$) δ: 40.46 (q, $^1J_{PB}$ = 65 Hz). ^{11}B NMR ($CDCl_3$) δ: −41.59 (qd, $^1J_{BH}$ = 96.4 Hz, $^1J_{PB}$ = 65 Hz). ^1H NMR ($CDCl_3$) δ: 0.65 (q, $^1J_{BH}$ = 96.4 Hz, 3H, BH_3), 1.21 (d, $^3J_{PH}$ = 13.1 Hz, 6H, CH_3), 1.69 (d, $^3J_{PH}$ = 12.8 Hz, 6H, –CH_3), 3.32 (broad s, 2H, –OH), 7.30–7.50 (m, 3H, $H_{arom.}$), 8.00–8.10 (m, 2H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 27.54 (qd, $^1J_{CH}$ = 128.1 Hz, $^2J_{CP}$ = 5.9 Hz, CH_3), 28.54 (qd, $^1J_{CH}$ = 128.2 Hz, $^2J_{CP}$ = 11.1 Hz, CH_3), 74.25 (d, $^1J_{CP}$ = 31.95 Hz, P–*C*–OH), 124.40 (d, $^1J_{CP}$ = 48 Hz, $C_{quat.}$–P), 127.30 (dd, $^1J_{CH}$ = 160.5 Hz, $^2J_{CP}$ = 9.3 Hz, C_{meta}), 130.60 (dd, $^1J_{CH}$ = 169.4 Hz, $^4J_{CP}$ = 2.4 Hz, C_{para}), 134.00 (dd, $^1J_{CH}$ = 171.4 Hz, $^3J_{CP}$ = 7.25 Hz, C_{ortho}). HRMS: $[M - 4\ H]^+$ found 270.095; calc. 270.0981.

6e: methylphosphine-borane **2** in benzene (2.5 M), propanone (3 equiv., 1.6 ml), 24 h at 60 °C. In the course of the reaction 0.4 equiv. of $BH_3 \cdot SMe_2$ is added in order to complex the free phenylphosphine which is released. $R_{f(CH_2Cl_2/Et_2O,9/1)}$ = 0.3, yield of pure product 70% (pale yellow solid). ^{31}P NMR ($CDCl_3$) δ: 40.2 (q, $^1J_{PB}$ = 65.2 Hz). ^{11}B NMR ($CDCl_3$) δ: −41.33 (qd, $^1J_{BH}$ = 93.6 Hz, $^1J_{PB}$ = 65.2 Hz). ^1H NMR ($CDCl_3$) δ: 0.30 (q, $^1J_{BH}$ = 93.6 Hz, 3H, BH_3), 1.31 (d, $^2J_{PH}$ = 9.8 Hz, 3H, P–C*H*$_3$), 1.40 (d, $^3J_{PH}$ = 12.2 Hz, 6H, C–CH_3), 1.56 (d, $^3J_{PH}$ = 12.1 Hz, 6H, C–CH_3), 3.46 (broad s, 2H, –OH). ^{13}C NMR ($CDCl_3$) δ: 2.75 (qd, $^1J_{CH}$ = 131.4 Hz, $^1J_{CP}$ = 34.4 Hz, P–*C*H$_3$), 27.68 (qd, $^1J_{CH}$ = 128.2 Hz, $^2J_{CP}$ = 6.15 Hz, C–*C*H$_3$), 27.98 (qd, $^1J_{CH}$ = 127.9 Hz, $^2J_{CP}$ = 9.6 Hz, C–*C*H$_3$), 72.34 (d, $^1J_{CP}$ = 33.4 Hz, P–*C*–OH).

4.6. Decomplexation of phosphine-borane adduct 5d and 6c

Triethylamine (1 equiv. for **5d** and 3 equiv. for **6c**) is slowly added to a 1 M solution of phosphine-borane **5d** or **6c** (1 mmol) in toluene. The mixture is stirred at room temperature and the reaction is monitored by ^{31}P NMR. After 1 day, the decomplexation is completed for **5d** leading to a complex mixture where phenylphos-

phine is the major product. For **6c**, after 5 days, a mixture of **6c** (44%), **4b** (40%) and **3b** (16%) is observed. All these compounds are identified by comparison with authentic samples (see above).

4.7. Hydroboration of benzaldehyde

Borane-dimethylsulfide (1 mmol, 0.1 ml) is slowly added to a molar toluene solution of benzaldehyde (3 equiv., 3.2 mmol, 0.3 ml). The mixture is stirred at room temperature for 24 h. The solvent is then removed under vaccum leading to the crude tribenzylboronate **7** in ca. quantitative yield. **7**: ^{11}B NMR ($CDCl_3$) δ: 18.5 (s). ^{1}H NMR ($CDCl_3$) δ: 5.30 (s, 6H, CH_2), 7.59–7.63 (m, 15H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$) δ: 65.9 (t, $^1J_{CH}$ = 144.3 Hz, CH_2), 127.2 (dm, $^1J_{CH}$ = 158.9 Hz, C_{ortho}), 127.8 (dm, $^1J_{CH}$ = 159.3 Hz, C_{para}), 128.8 (dm, $^1J_{CH}$ = 160.7 Hz, C_{meta}), 140.4 (m, $C_{quat.}$).

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